Oxygen-Vacancy-Induced Orbital Reconstruction of Ti Ions at the Interface of $LaAlO_3/SrTiO_3$ Heterostructures: A Resonant Soft-X-Ray Scattering Study

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Resonant soft-x-ray scattering measurements have been performed to investigate interface electronic structures of ($LaAlO_3/SrTiO_3$) superlattices. Resonant scattering intensities at superlattice reflections show clear evidence of degeneracy lifting in t_{2g} states of interface Ti ions. Polarization dependence of intensities indicates the energy of d_{xy} states is lower by $\sim$1 eV than two other t_{2g} states. The energy splitting is insensitive to epitaxial strain. The orbital reconstruction is induced by oxygen vacancies and confined to the interface within two unit cells, indicating charge compensation at the polar interfaces.

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The recent discovery of conducting interfaces between two insulating oxides opened the door to oxide electronics [1]. A prominent example is the interface between $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) which manifests not only metallicity [2], but also magnetism [3] and superconductivity [4]. Recent findings of a coexistence of magnetism and superconductivity [5] make this interface more interesting. The origin of extra electrons required for the two-dimensional electron liquid phenomena is closely related to compensation of charge imbalance at the LAO/STO (001) interface [6]. Since interface charge density is pivotal for the performance of oxide electronics devices, a mechanism of the interface charge compensation has been a subject to clarify and several mechanisms have been proposed [6–8]. Among them, oxygen vacancy has been considered as one of the natural ways to compensate for polar discontinuity not only for the LAO/STO interface, but also for other oxide polar interfaces such as ferroelectric-dielectric interfaces [9]. Moreover, a recent theoretical result suggested that oxygen vacancies induce orbital reconstruction of Ti $3d$ states and the reconstructed t_{2g} states provide interface magnetic moments required for the coexistence of ferromagnetism and superconductivity [10]. Though the interface states induced by oxygen vacancy are considered to play such a crucial role in the interesting phenomena, they have never been observed experimentally. In this Letter, we present results of our resonant soft-x-ray scattering (RSXS) experiments which demonstrate orbital reconstruction and charge compensation induced by oxygen vacancy at the LAO/STO polar interface.

RSXS can be described by a second order perturbation process of excitation and deexcitation between core electrons and empty states. Therefore, its intensities inherently contain spectroscopic information. In addition, since the amplitudes of x rays scattered by interfaces or bulk regions strongly depend on the momentum transfer, we can choose the superlattice reflections, which are sensitive to interface or bulk properties, as demonstrated by Smadici *et al*. for a ($LaMnO_3/SrMnO_3$) superlattice [11].

We conducted polarization dependent RSXS experiments to investigate interface electronic structures of Ti t_{2g} orbitals in (LAO/STO) superlattices, separately grown on STO and $NdGaO_3$ (NGO) substrates. Identical superlattice structures, which are ten repeating units of twelve LAO and six STO unit cells $(LAO_{12}/STO_6)_{10}$ on a LAO_{12} buffer layer, were grown on both a TiO_2-terminated STO and a NGO substrate by pulsed laser deposition at 700 °C in 10^{-2} Torr of O_2. Details on the superlattice preparation and growth parameters can be found elsewhere [12,13]. Note that the oxygen partial pressure is about 4 orders of magnitude higher than the values typically employed in some previous reports [2,14]. Since the oxygen pressure was confirmed to be high enough to suppress oxygen vacancies during growth process [13], it was used to minimize the effects of low pressure growth, as often seen in spectral investigations such as electron energy loss spectroscopy [15] and in coherent Bragg rod analysis for electron density profile [13]. Both samples were highly insulating. By monitoring the intensity oscillations of reflection high-energy electron diffraction specular spot, the bilayer thickness and their ratio (d_{LAO}: d_{STO} = 12:6) was designed to achieve high sensitivity of the (003) and (004) superlattice reflections to the electronically reconstructed interfaces as described below. As shown in Fig. 1(a), hard x-ray diffraction measurements confirmed our superlattices are fully strained preserving high crystallinity. Superlattice

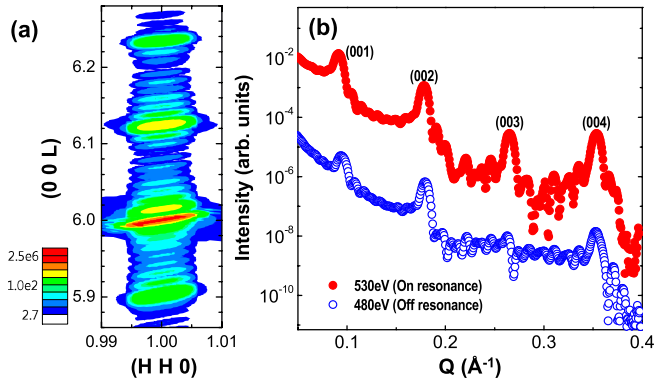

FIG. 1 (color online). (a) A reciprocal space map of x-ray diffraction intensities around (116) Bragg reflection for a (LAO/STO) superlattice on a NGO substrate. (b) Measured specular x-ray reflectivities for a (LAO/STO) superlattice on a STO substrate at a resonance energy of O K edge, 530 eV (solid red circles), and at an off-resonance energy of 480 eV (open blue circles). The data are vertically shifted for comparison.

reflections as well as total-thickness oscillations were also clearly observed. The intensity of the (003) reflection in x-ray reflectivity curve was strongly suppressed at an off-resonance energy, as shown in Fig. 1(b), which ensured the high quality of our superlattice samples.

RSXS measurements were conducted at beamline 2A of the Pohang Light Source. An ultra-high-vacuum compatible two-circle diffractometer was used with a photodiode as its detector for the measurement [16]. Polarization of the incident x rays was controlled using an elliptical polarization undulator, while both polarizations of the scattered x rays were integrated. The scattering vector along the surface normal was parallel to the multilayer growth direction and [001] crystallographic axis of the substrates. Note that, for $\sigma(\pi)$ polarization, the electric field direction of x rays was perpendicular (parallel) to the scattering plane. Energy profiles of superlattice reflections were taken at room temperature.

A repeating unit of our superlattice samples makes the contribution of the interface to a scattering intensity dominant at the (004) reflection. In the kinematical approximation, the scattered intensity, I, and the structure factor, $S(\vec{q})$, with the momentum transfer, $\vec{q}$, is given by

$$I \propto |S(\vec{q})|^2 = \left| \sum_j f_j e^{i\vec{q}\cdot\vec{r}_j} \right|^2, \quad (1)$$

where f_j and $\vec{r}_j$ are the scattering factor and position of the jth atom in a unit cell. Similarly, when f_{LAO} and f_{STO} are defined as scattering factors of LAO and STO unit cells, respectively, the structure factor of (00 L) reflection for an ideal superlattice can be written as

$$S(00L) = f_{\mathrm{int\,STO}} + \sum_{k=1}^{5} f_{\mathrm{STO}} e^{i(2\pi kL/18)} + \sum_{k=6}^{16} f_{\mathrm{LAO}} e^{i(2\pi kL/18)} + f_{\mathrm{int\,LAO}} e^{i(34\pi L/18)}, \quad (2)$$

where k is the index for kth unit cell along the vertical direction. Here it is assumed, for simplicity, that electronic reconstruction occurs only at the $AlO_2 - LaO/TiO_2 - SrO$ interfaces whose scattering factors are represented by $f_{\mathrm{int\,LAO}}$ and $f_{\mathrm{int\,STO}}$. This assumption is justified by the previous reports that only the n-type interfaces exhibit a conducting behavior [2] and x-ray energy was chosen to probe Ti $3d$ states selectively [17]. Then the resonant enhancements of f_{intLAO} and f_{LAO} are not significant, and the resonant scattering structure factors for (001), (003), and (004) reflections can be simplified as

$$\begin{aligned} S(001) &= f_{\mathrm{int\,STO}} + (2.2 + 3.8i) f_{\mathrm{STO}} \\ S(003) &= f_{\mathrm{int\,STO}} - f_{\mathrm{STO}} \\ S(004) &= f_{\mathrm{int\,STO}} + (0.26 + 0.46i) f_{\mathrm{STO}}. \end{aligned} \quad (3)$$

As previously seen by others [11,18], the resonant enhancement of (003) reflection directly shows that the electronic reconstruction occurs at the interface. However, it is difficult to characterize quantitatively the reconstructed electronic structure using the (003) reflection because the reflection represents only the difference between contributions of the bulk and interfaces as shown in Eq. (3). Unlike the (003) reflection, the structure factors of (001) and (004) reflections dominantly represent contributions from the bulk and interfaces, respectively. Therefore, this fact allows us to characterize the electronic structures of the bulk and interface separately.

Figure 1(b) shows x-ray reflectivity of a (LAO/STO) superlattice on a STO substrate. At the resonance energy of O K edge, 530 eV, one can see clearly the enhancement of (003) reflection which is a forbidden peak at an off-resonance energy of 480 eV. The resonant enhancement of (003) reflection intensities is direct evidence of the reconstructed electronic structure at the interfaces.

Detailed information on the electronic structure of interfaces can be obtained using the energy dependence of RSXS intensities. X-ray absorption spectroscopy (XAS) spectra near the O K edge have been often measured to investigate transition metal $3d$ orbitals hybridized with ligand p states [17]. XAS spectra of STO show peaks around 531 and 533.3 eV, as shown in Fig. 2(a), which correspond to states coupled to Ti t_{2g} and e_g orbitals, respectively. Then, O $2p$ states hybridized with the Ti t_{2g} orbitals can be selectively investigated by analyzing energy profiles of RSXS around 531 eV. Energy profiles of superlattice reflections near the O K edge for the sample on STO are shown in panels of Figs. 2(c), 2(e), and 2(g), while data for the sample on NGO are shown in panels of (d),(f) and (h). The results present three main features: first, the profiles are combinations of single- and double-peak structures. Second, the double-peak structure shows an energy splitting of ~1 eV for σ-polarization in Figs. 2(g) and 2(h). Third, RSXS intensities show polarization dependence, and the ratios between peak intensities of the double-peaks are different for σ and π polarizations.

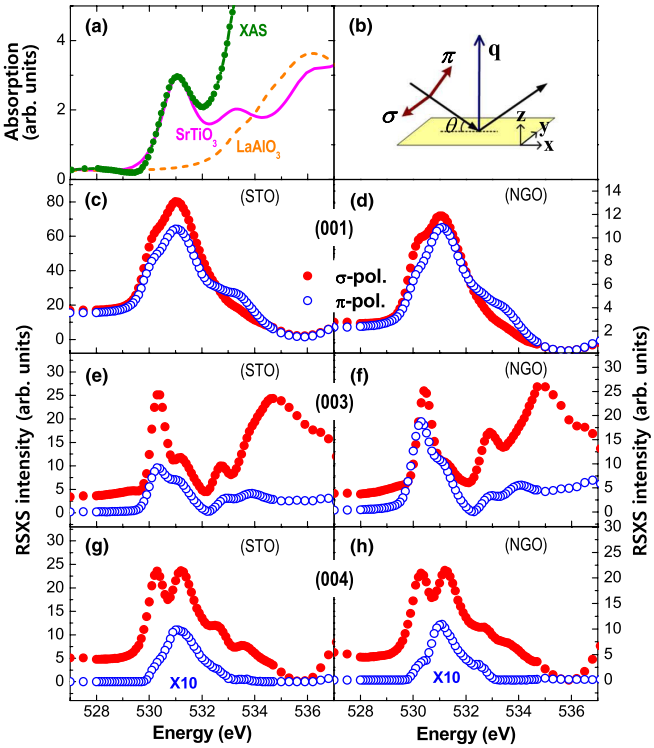

FIG. 2 (color online). (a) Experimental XAS data for our sample (green circles). A solid line is a guide for eyes. XAS spectra of bulk STO (purple solid line) and electron energy loss spectra of LAO (orange broken line) from published data [6,25]. The energy reference were shifted. (b) A schematic diagram of the scattering geometry. (c)–(h) Energy dependence of RSXS intensities for the superlattice reflections at O K edge for the samples grown on STO and NGO substrates: (c), (e) and (g) for the STO substrate and (d), (f) and (h) for the NGO substrate. Solid red circles and open blue circles are experimental data for σ and π polarizations, respectively.

The (001) reflection exhibits an almost single-peak structure around 531 eV whereas the (004) reflection shows a double-peak structure with a splitting of $\sim$1 eV [19]. Since the (001) and (004) reflections dominantly present the bulk and interface features, respectively, these profiles show that degeneracy of t_{2g} states is lifted only at the interfaces. The (003) reflection also shows a clear distinction between the bulk and interface structure factors. The result confirms the bulk portion dominates in STO sublayers, and it also shows the degree of confinement for the orbital reconstruction near the interface. Considering STO sublayers consist of only six unit cells, it is clear that degeneracy-lifted t_{2g} states are confined to the interfaces within two unit cells, at most.

Our experimental geometry is schematically illustrated in Fig. 2(b). The electric field of σ-polarized x-ray photons is parallel to y axis, where we consider x, y, and z axes along the crystallographic axes of the substrate with the z axis perpendicular to the interface. Assuming the energy of the in-plane state (d_{xy}) is different from the degenerate value of out-of-plane states (d_{xz} and d_{yz}), the scattering factors of Ti ions near O K edge for σ and π polarizations can be expressed as

$$f_\sigma = F_{\text{in plane}} + F_{\text{out of plane}}$$
$$f_\pi = -F_{\text{in plane}}\sin^2\theta + F_{\text{out of plane}}(2\cos^2\theta - \sin^2\theta), \quad (4)$$

where θ is the incident angle of the x rays. $F_{\text{in plane}}$ and $F_{\text{out of plane}}$ represent the resonant enhancements of transitions to O $2p$ states hybridized with in-plane and out-of-plane orbitals, respectively. As shown in Eq. (4), the ratio between RSXS intensities corresponding to in-plane and out-of-plane states strongly depends on θ for π polarization but not for σ polarization. For the (004) reflection, θ is approximately 40° and the ratio for π polarization is much less than that for σ polarization, by a factor of $[\sin^2\theta/(2\cos^2\theta - \sin^2\theta)]^2$ ($\sim$ 0.3). From Figs. 2(g) and 2(h), it is clear that the low- and high-energy peaks correspond to O $2p$ states hybridized with in-plane d_{xy} and out-of-plane t_{2g} states of the Ti ions, respectively. The observed polarization dependence also excludes the possibility of change in binding energy at the interface as an origin of the splitting previously suggested by others [19].

To study the effect of epitaxial strain on the crystal-field splitting, RSXS measurements on another superlattice sample grown on a NGO substrate were performed and the results are presented in panels of Figs. 2(d), 2(f), and 2(h). Lateral lattice mismatch between the bulk values of NGO and STO is about 0.04 Å, which is almost equivalent to the vertical elongation of interface STO unit-cells estimated by surface x-ray scattering experiment for a LAO overlayer on a STO substrate [7]. Crystal-field splitting is generally sensitive to the change in the positions of nearest neighbor ions [20] and the epitaxial strain dependence on electrical conduction has been reported by others [21]. Therefore, a change in the energy splitting is expected. However, the RSXS spectra on both samples were surprisingly identical, which indicates the observed splitting is not related to distortions of interface octahedra due to the strain. The splitting of $\sim$1 eV is also too big for orbital reconstruction due to the distortion. Although a similar low-energy d_{xy} state has been reported for the interface between $LaTiO_3$ and $LaAlO_3$ [22], it was attributed to asymmetric bonding at the interface which depends on strains and contradicts with our observation. Therefore, it is concluded that the low-energy d_{xy} state results mainly from some severe disruption such as oxygen vacancy and its correlation character.

The energy splitting of $\sim$1 eV estimated from our RSXS measurements near O K-edge is much larger than those of XAS measurements by Salluzzo *et al.* ($\sim$ 50 meV) [23]. Since the XAS measurements were done at Ti L edges, RSXS measurements at the Ti L edges were also conducted for comparison and the results are shown in Fig. 3. Unlike the O K edge, the energy profile of RSXS at Ti L edges

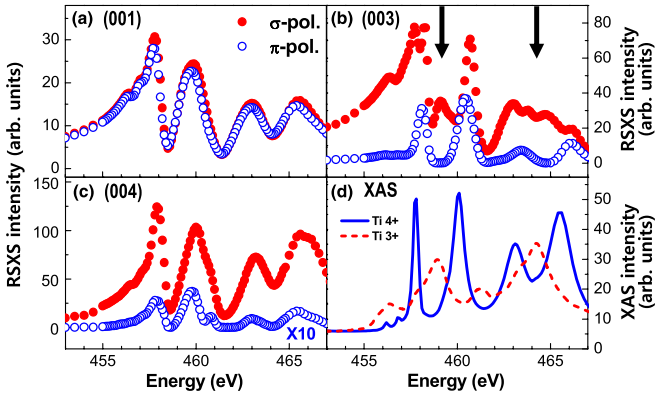

FIG. 3 (color online). (a)–(c) Energy dependence of RSXS intensities of the (001), (003), and (004) superlattice reflections at Ti L-edges for the sample grown on STO. Solid red circles and open blue circles are experimental data for σ and π polarizations, respectively. (d) XAS results for Ti^{4+} (solid blue line) and Ti^{4+} ions (broken red line) from published data of others [26,27].

does not directly represent the unoccupied density of states because strong final state effects in the transition result in multiplet states and distort the profile. Nevertheless, fingerprints of electronic reconstruction can be observed. The RSXS profile for the (001) reflection shows a characteristic feature of Ti^{4+} ions as presented in Fig. 3(a). The (003) reflection intensities in Fig. 3(b) show the difference between the bulk and interface Ti $3d$ states. Most noticeable is the enhanced intensity between t_{2g} and e_g peaks as pointed by arrows, a characteristic of Ti^{3+} ions, which is the evidence of extra electrons at the interface. However, the (004) reflection intensities in Fig. 3(c) do not show such a distinctive feature. It is remarkable that an important feature of the interface is not noticeable at the interface-sensitive (004) reflection while it is observed in the (003) reflection. The result strongly implies a low density for the extra electrons. The density is so low that the overall features of the interface is similar to the bulk. On the other hand, the difference-sensitive (003) reflection represents small deviations from the bulk, rather than the inherent features of the interface. The deviations have their own peaks shifted with respect to profiles of other reflections and XAS, as seen in Fig. 3(b).

There is a considerable difference between RSXS profiles of our (LAO/STO) samples at O K and Ti L edges. At the (004) reflection, the characteristic feature of interface orbital reconstruction is dominant at the O K edge even at its low density, while it is not noticeable at the Ti L edges. The difference demonstrates that the reconstructed orbital is a localized state since resonance enhancement is greater for the transition of a core electron to a localized state than for that to an extended state. However, the strong final state effect at Ti L edges not only reduces the contrast between resonance enhancements but also redistributes oscillator strength of the transition into the multiplet states, which makes the orbital reconstruction less noticeable.

Pavlenko *et al*. recently proposed the reconstruction of t_{2g} orbitals induced by oxygen vacancies to explain the coexistence of ferromagnetism and superconductivity at the LAO/STO interface [10]. According to the model, the energy splitting of d_{xy} orbitals takes place at the interface due to extra electrons from oxygen vacancies. The low-energy state is spin polarized and its energy level is $\sim$1 eV lower than those of other t_{2g} states. The reconstructed orbital states are mainly localized and do not contribute much to the transport properties. Though spin polarization of the induced state has not been checked, the agreement between theoretical calculation and our results is so excellent that our results provide the experimental evidence for oxygen vacancy-induced states.

Oxygen vacancy has been recently proposed to explain interface charge compensation of polar materials [9], but the mechanism has not been experimentally observed. As mentioned above, our results demonstrate that interface states are induced by oxygen vacancy for the (LAO/STO) superlattice samples. Considering high diffusivity of the vacancy in STO as well as the 6 unit cell thickness of the STO sublayers, the narrow confinement of interface states within two unit cells is unexpected. We attribute the confinement mainly to charge compensation for polar discontinuity at the interfaces, since extrinsic mechanisms such as oxygen deficiency or bombardments of energetic particles during growth process cannot produce such narrow confinements [24]. However, the low density of Ti^{3+} ions indicates partial compensation at the interface.

In conclusion, the localized d_{xy} state of interface Ti ions, which was induced by oxygen vacancy, was observed from our RSXS measurements for (LAO/STO) superlattices. It had an energy level lower than other t_{2g} states by $\sim$1 eV. The energy splitting was robust and insensitive to epitaxial strain. A low concentration of Ti^{3+} ions were also observed. The states were confined to the interfaces within two unit cells. Our results show excellent agreement with the oxygen vacancy model. They also provide the experimental evidence for the partial compensation of polar discontinuity by oxygen vacancies at the LAO/STO interface. Since the interface compensation is a generic phenomenon in other oxide polar interfaces, RSXS can be used as a powerful probe to characterize them.

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